Stability study in organic solar cells based on PTB7:PC71BM and the scaling effect of the active layer

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Lifetime
Alternative electrodes
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A B S T R A C T

Performance and stability of organic photovoltaic cells (OPVs) based on the benchmark bulk heterojunction PTB7:PC71BM and the alloy Field's metal (FM) as top-electrode deposited by doctor blade technique, are fully studied when the active area is scaled by a factor of 25. Power conversion efficiency (PCE) of small active area (0.09 cm2) devices resulted in 7.4 ± 0.8%, which is within the range of values commonly achieved for devices comprising Al as traditional, costly and nonstable top-electrode. However, PCE decreased 60% for scaled OPVs (2.25 cm2). Studies of stability as a function of the active area were performed in accordance with the ISOS-L1 (laboratory simulation of constant lighting) and ISOS-D1 (shelf storage) protocols for devices tested in air and without encapsulation. The time to reach 50% of the initial PCE (T50) is about 14 h and 2000 h under ISOS-L1 and ISOS-D1 protocols, respectively, with a tendency of stability improvement for scaled devices. A whole PV analysis through the single diode model, impedance spectroscopy, and light beam induced voltage (LBIV) measurements is presented. Our results are a good indication that FM top-electrode, of cheap and easy deposition under vacuum free conditions, provides an acceptable photovoltaic performance after scaling the active area.

1. Introduction

Despite the technology of organic photovoltaic cells (OPVs) based in the bulk heterojunction (BHJ) architecture offers many advantages, the integration of devices that can be commercially available still remains as a challenge (Kang et al., 2016). For instance, two of the main limitations of the current devices in which high PCE (∼ 11–13%) has been achieved (National renewable energy laboratory, 2017) are the poor environmental stability and the small size of the active area. Hence, further research efforts to study the stability and improving the properties of scaled devices are essential to make progress in this technology. In general, diverse degradation processes occur simultaneously in layers and interfaces of OPVs, each one influenced by different factors such as moisture, oxidation, materials aggregation, and others (Cao et al., 2014; Djurisic et al., 2016). With the use of standard counter-electrodes (Al, Ag, Ca, etc.), oxidation occurs on top side and internal interfaces (Lloyd et al., 2009; Turak, 2013); this oxidation limits device stability through increments in the series resistance and reducing the fill factor (FF). Williams et al. (2013) carried out an exhaustive study of the interfacial layer effects on the device stability; their results showed that the active layer/metal interface limits the OPVs photo-stability, however, the insertion LiF or Liacac as electron extraction layer (EEL) improved the photostability. The stability of different electron-donor polymers and diverse electron-acceptor molecules as well as their blends has been also studied by different groups for a wide variety of architectures (Cheng and Zhan, 2016).

Because its efficient photovoltaic properties, the low bandgap semiconducting polymer Poly[(4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2 ethylhexyl)carbonyl]thieno][3,4-b][thiophenediy]] (PTB7) is thoroughly employed for developing efficient OPVs with the blend PTB7:PC71BM as active layer (He et al., 2012; Guerrero et al., 2013; Etzebarria et al., 2014; Ebenhoeh et al., 2015). However, the stability of PTB7:PCBM-based devices is very susceptible to fabrication procedures and the environment (Arbad...
et al., 2014). For instance, the use of the solvent additive 1,8-diiodooctane (DIO) can reduce device stability directly, since PTB7 polymer chains could be more exposed to degradation factors due to a diminishing in the shielding layer of PC_{71}BM formed under the metal electrode (Kim et al., 2015). The role of PC_{71}BM in photo-induced reactions that cause deterioration of the electron transport properties and boost the formation of electron trapping states within the BHJ has been also studied (Bartesaghi et al., 2016). In spite of these and other intrinsic mechanisms of instability when the blend PTB7:PC_{71}BM is exposed to air, light, or both, diverse strategies can be implemented to alleviate its degradation, either using encapsulation methods (Abdel-Fattah et al., 2014) or the inclusion of humidity-resistant materials, namely PVK (Álvarez-Fernández et al., 2016). The size of the active area is another factor that might influence the stability of the blend PTB7:PC_{71}BM, however, the knowledge of the effect of scaling the area of PTB7:PC_{71}BM active layer on the stability of OPVs has not been investigated. For other blends, i.e., P3HT:PC_{71}BM, some studies showed that the photovoltaic stability decay slower as the active area is increased (Wang et al., 2011).

In this work, we investigate the photovoltaic performance and stability of OPVs based on the blend PTB7:PC_{71}BM and the effects induced when the active area is scaled by a factor of 25. The employed architecture was ITO/PEDOT:PSS/PTB7:PC_{71}BM/PFN/Field’s metal (FM). FM is an alternative air-stable top electrode, it has been deposited by dropping and doctor blade technique at 90 °C under normal laboratory atmosphere (Pérez-Gutiérrez et al., 2017). The composition of this eutectic FM alloy is Bi/In/Sn (32.5%, 51%, 16.5%), with a melting point of 62 °C (Rotometals, 2017) and electrical resistivity of 5.2 × 10^{-7} Ω-m (MatWeb, 2017); the work function of this electrode was determined theoretically (Nolasco et al., 2014) and in situ measured (Reese et al., 2016) and resulted in 4.47 eV, and also measured through the Kelvin probe technique (Pérez-Gutiérrez et al., 2016) and resulted in 4.2 eV. The attention was focused on the factors that determine the degradation in non-encapsulated devices kept either under continuous illumination or in dark storage both in normal room conditions, using the first level of the established protocols ISOS-L1 (laboratory simulation of constant lighting) and ISOS-D1 (shelf storage) (Reese et al., 2011). Evaluation of devices performance using these protocols was carried out through density-current-voltage (J-V) measurements, impedance spectroscopy and light beam induced voltage (LBIV) maps (Krebs et al., 2011). The use of these methods allowed us to quantify changes in the electrical parameters that characterize the performance of devices after photo-degradation and scaling the active area. As for OPVs stability, our results show that FM is a good alternative to the common and costly evaporated top electrodes. This alloy shows less oxidation compared with standard metals used as counter-electrodes, providing similar or improved stability than in previous reports on PTB7:PC_{71}BM-based devices. Additionally, when the device active area is scaled, FM does not introduce significant losses since increments in resistive effects are mostly associated to scaling the anode (ITO) surface and possible defects in the active film introduced during fabrication process.

2. Experimental section

2.1. Materials and device fabrication

Polymer PTB7 and (6,6)-Phenyl C71-butyric acid methyl ester (PC_{71}BM) were purchased from 1-Materials. Glass/ITO substrates with a sheet resistivity of 4–10 Ω/□ were purchased from Delta Technologies. PEDOT:PSS was acquired from Heraeus-Clevulis, the alcohol/water soluble conjugated polymer poly[(9,9-bis(3’-N,N-dimethylamino)propyl)-2,7-fluorene-alt-2,7-(9,9-dioctyfluorene) (PFN) was acquired from 1-Material, and the eutectic alloy Field’s metal (FM) was obtained from Rotometals. Glass/ITO substrates (2.5 × 3 cm^2) were cleaned with a soap solution, acetone, ethanol and isopropanol in ultrasonic baths and dried immediately. Afterward they were treated with UV-Ozone for 10 min. A layer of PEDOT:PSS was deposited by spin–coating at 4500 rpm (~40 nm thickness) and subsequently the substrates were annealed at 80 °C for 15 min. A solution of PTB7:PC_{71}BM (1:1.5 wt% ratio, ~30 mg/ml) in chlorobenzene with 3% of 1,diiodooctane was spin–coated under N_{2} atmosphere to achieve an active layer with thickness of ~100–110 nm; after active layer deposition the substrates were dried at 80 °C for 10 min. A PFN film was coated on top of the active layer by spin coating at 5500 rpm (~8 nm thickness) in normal atmosphere. Some studies showed that PFN is able to form a dipole interface that favor the electron extraction (Huang et al., 2004; He et al., 2012). The active area in devices was delimited using a procedure described in our previous report (Barreiro-Argüelles et al., 2017), to obtain devices of 0.09 cm^2 and 2.25 cm^2. Finally, FM pellets were melted at 90–100 °C and deposited as counter-electrode (top electrode) on top of the active layer by using a doctor blade machine (Elcometer 4340 motorized); during the deposition of the top electrode, devices were kept heated (~90 °C) using a hot plate adapted to the doctor blade machine. Then, samples were cooled down to room temperature. The OPVs were not encapsulated. The cell architecture is schematically presented in Fig. 1.

2.2. Device characterization and degradation protocols

Characteristic J-V curves were obtained using a Keithley 2450 source-meter and a solar simulator class AAA (Scientech ECSS150) to provide AM1.5 of illumination condition (1000 W/m^2). The AM1.5 condition was calibrated using a silicon reference cell (model 15,151 acquired from Abet technologies) with an accuracy of 6%. Impedance response was measured using a potentiostat/galvanostat system (PARTAT 2273). Impedances were measured over the frequency range 1 kHz–1 MHz, with an oscillation amplitude of 10 mV rms, always recorded under illuminated conditions over different DC bias from 0.0 to 0.5 V (nearly the V_{max} value). Impedance spectra were simulated using the ZView software and an equivalent circuit. LBIV experiments were carried out using a setup implemented in the laboratory with a 375 nm laser diode and a computer controlled XYZ-stage (Pérez-Gutiérrez et al., 2016). The laser power (spot diameter = 7 μm) hitting directly on the OPVs under tests was 1.3 μW, equivalent to an intensity of 3.3 W/cm^2. This value is certainly larger in comparison with the AM1.5 condition (100 mW/cm^2 = 0.1 W/cm^2). Nevertheless, LBIV measurements were intended to show superficial fabrication defects and stability of the generated signal through the use of monochromatic light. Noticed that typically, LBIV experiments are performed with a laser intensity larger than the corresponding to AM1.5 (Navas et al., 2010). Immediately after fabrication, all devices were first characterized by J-V measurements, impedance spectroscopy and LBIV maps, all of them under normal room conditions.

In order to obtain the rate at which devices lose their properties, all characterizations were conducted according to ISOS-L1 (laboratory simulation) and ISOS-D1 (shelf storage) testing protocols (Reese et al., 2011). The specifications of these protocols can be consulted in Table S1 and Table S2 in Supporting Information. To apply the first protocol, devices were chosen randomly from the prepared batches and placed under continuous illumination (AM1.5). Their characteristic J-V curves were obtained every hour; after each J-V characterization, OPVs were kept in open circuit condition until the next measurement. In addition, characterization through impedance spectroscopy and LBIV maps were carried out at 0, 12 and 24 h of initiated the protocol. For the second protocol, we again chose devices randomly for characterization; in this case they were stored in darkness and various J-V plots were achieved during the first days and then characterization was spaced to approximately every 250 h. Since the OPVs were tested at the normal laboratory conditions, temperature and humidity were monitored every hour for the first protocol and every day for the second one.
3. Results and discussion

3.1. Initial performance

Characteristic $J-V$ curves for the initial performance of OPVs with two different active areas are shown in Fig. 2. OPVs with 0.09 cm$^2$ of active area are characterized by the following average photovoltaic parameters (from six samples): short-circuit current density ($J_{sc}$) of 17.9 mA/cm$^2$, open circuit voltage ($V_{oc}$) of 0.75 V, fill factor (FF) of 0.55 and power conversion efficiency (PCE) of 7.4%. A summary of these photovoltaic characteristics is presented in Table 1. Small area devices were also characterized through incident photon to charge carrier efficiency EQE (IPCE) experiments. Fig. S1 displays the obtained EQE spectra for a set of samples; these spectra are characteristic of OPVs comprising PTB7:PCBM as active films (He et al., 2012). EQE spectra can be utilized to calculate $J_{sc}$ using the expression:

$$J_{sc} = \int q \text{IPCE}(\lambda) N_{ph}(\lambda) d\lambda$$

(Kumar et al., 2015) where $q$ and $N_{ph}(\lambda)$ are the electron charge and the photo flux intensity at the wavelength $\lambda$, respectively. The experimental data shown in Fig. S1 results in $J_{sc} = 17.7 \pm 0.3$ mA/cm$^2$. This value is in very good agreement with the average value obtained through $J-V$ curves (17.9 ± 1.2 mA/cm$^2$).

Table 1 also presents the maximum PV values achieved for the best OPVs, i.e., a maximum $J_{sc} \sim 19.3$ mA/cm$^2$ was obtained although such device exhibits a relatively limited FF of 0.57 that in turn produces a maximum PCE of 8.2%. As we can see, the average PV performance of these small active area devices are comparable to PTB7-based OPVs commonly reported in literature (He et al., 2012; Kim et al., 2015; Tada, 2014; Qi et al., 2015). However, when the active area is scaled up 25 times (to 2.25 cm$^2$), there is a notable decrease of PCE leading to an average value of 2.8%; this value is approximately 37% of the PCE value corresponding to devices with 0.09 cm$^2$ of active area. Likewise, $J_{sc}$ and FF values were reduced in 65% and 56%, respectively. In contrast, the parameter $V_{oc}$ remained practically unchanged. Notice that the parameters $J_{sc}$, PCE and FF exhibited less variation in OPVs with larger active area. Better reproducibility on the performance of scaled devices can be associated to the fact that fabrication defects and inherent material deficiencies tend to be averaged as the size of active area is increased.

Table 1 also shows the influence of scaling the active area on the series ($R_s$) and parallel ($R_p$) resistances. Such resistances were estimated by fitting the $J-V$ curves to an equivalent circuit for OPVs (single diode model) (Kippelen and Brèdas, 2009). Examples of fitted curves can be consulted in supporting Information (see Fig. S2). For the case of $R_s$, obtained under illumination, there is a significant increment of 7.4 times after scaling the area, while in the case of $R_p$ the increment is just 16%. It is well known that resistances play an important role in limiting the FF (Nelson, 2003). Based in previous reports for devices in which the architecture is constructed with evaporated counter-electrodes (Al, Ag), the FF decreases almost linearly with the active area due to the dominant contribution of series resistance from ITO (Jeong et al., 2011; Xiao et al., 2015). The typical electrical conductivity of sputtered ITO films is three orders of magnitude smaller ($\approx 10^4$ S/m) compared with metals commonly used as top electrodes (Al = 3.5 × 10$^7$ S/m, Ag = 6.3 × 10$^7$ S/m) (Hosono et al., 2002) and two orders of magnitude smaller compared to the top electrode used in this work (FM $\sim 1.9 \times 10^6$ S/m) (MatWeb, 2017). Then, we hypothesized that one of the main reasons for the FF reduction in OPVs of large area is ascribed to the series resistance increasing generated from scaling the ITO active area. To elucidate this assumption, we performed four-point probe...
resistivity measurements. Indeed, the values obtained for films of FM and ITO were 0.0018 Ω/□ and 10.4 Ω/□, respectively. Also, other factors could reduce the FF due to changes in resistances as a consequence of area scaling, for instance, current density losses attributed to irregularities in morphology, and lack of uniformity in thickness (Jeong et al., 2011; Agrawal et al., 2016). By using LBIV method we can see how the performance of devices is affected by possible lack of uniformity or electrode deposition (these results will be presented in the following sections).

3.2. Stability test

3.2.1. Laboratory simulation (ISOS-L1 protocol)

OPVs were irradiated by a solar simulator over a period of 24 h using the ISOS-L1 protocol at normal laboratory conditions. In order to monitor stability, J-V curves were obtained every hour; after each J-V characterization devices were kept at open circuit conditions until the next measurement. During the implementation of this protocol the temperature and the relativity humidity were 20.6 ± 1 °C and 47.5 ± 2.5%, respectively.

Changes of photovoltaic parameters as a function of time are shown in Fig. 3. Examples of characteristic J-V plots for both small (0.09 cm²) and scaled (2.25 cm²) active areas obtained at 0, 12 and 24 h under continuous illumination are presented in Fig. S3. It can be observed in Fig. 3a that reduction in Jsc at early times is more significant in large area devices than in small ones, reaching 80% of the initial performance in approximately 3 h, while for small area devices such value is reached in the double of time (6 h). Despite this difference in stability at the initial times, the tendency is that both devices reach 50% of the initial Jsc value after 20 h of continuous illumination. Voc decays slightly independently of the size of active area (Fig. 3b). In regards to FF (Fig. 3c), small area devices exhibit a monotonic decay for the first 13 h followed by stabilization to 75% of the original value. Remarkably, FF value tends to be more stable for large area devices. Further, such parameter exhibits an increment of approximately 15% after 6 h and its value after 24 h is not less than the one measured at the initial time. In overall, devices under continuous illumination reach 50% of the initial PCE (T50) in about 14 h for both active areas (Fig. 3d). Recently, shorter stabilities (T50 ~ 5 h) have been observed in encapsulated PTB7-based devices (Upama et al., 2016) with inverted architecture and small area

Table 1
Photovoltaic performance of OPVs with two different active areas. Numbers in parenthesis represent the average value of 6 tested devices. The values out of the parenthesis represent the device with the best performance. Rs and Rp were obtained for OPVs under illumination.

<table>
<thead>
<tr>
<th>Photoactive area [cm²]</th>
<th>Jsc [mA/cm²]</th>
<th>Voc [V]</th>
<th>FF</th>
<th>PCE [%]</th>
<th>Rs [Ω·cm²]</th>
<th>Rp [Ω·cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.09</td>
<td>19.3 (17.9 ± 1.2)</td>
<td>0.74 (0.75 ± 0.01)</td>
<td>0.57 (0.55 ± 0.03)</td>
<td>8.2 (7.4 ± 0.8)</td>
<td>4.3 (4.5 ± 0.4)</td>
<td>306.1 (263.4 ± 59)</td>
</tr>
<tr>
<td>2.25</td>
<td>12.1 (11.8 ± 0.4)</td>
<td>0.76 (0.75 ± 0.01)</td>
<td>0.33 (0.31 ± 0.02)</td>
<td>3.1 (2.8 ± 0.2)</td>
<td>32.8 (33.6 ± 1)</td>
<td>313.8 (308.1 ± 8)</td>
</tr>
</tbody>
</table>

Fig. 3. Evolution of the normalized parameters: (a) short circuit current density, (b) open circuit voltage, (c) fill factor and (d) power conversion efficiency for OPVs with active areas of 0.09 cm² (filled squares) and 2.25 cm² (open circles) under ISOS-L1 testing protocol. The average values and error bars were calculated from the parameters obtained from six devices of 0.09 cm² and three devices of 2.25 cm²; each device was tested in three independent experimental runs.
Although the combination of such architecture with the use of PTB7 of higher molecular weight (M_n = 215 700 g/mol, M_w/ M_n = 2.46) was also recently proved as successful strategy to enhance the stability (T_{50} = 96 h) (Ding et al., 2016). It is worth notice that in these cited works the inverted architecture is used as a well-known strategy to improve stability (Cheng and Zhan, 2016; Etxebarria et al., 2014). To the best of our knowledge, there are no previous studies for PTB7-based OPVs with non-inverted architecture tested under continuous illumination. As it can be seen, the value of T_{50} ~ 14 h achieved in our OPVs (fabricated with direct architecture, without encapsulation, and having FM as top electrode) is in the range of stabilities observed for PTB7-based OPVs comprising inverted architectures and standard counter-electrodes.

Under the ISOS-L1 protocol we can monitor how photo-degradation processes impact on the stability of the equivalent circuit parameters for OPVs. Table 2 shows the extracted parameters for our OPVs using the single diode model at 0, 12 and 24 h of illumination. The J-V curves used to extract these parameters were obtained under both dark (photocurrent J_{ph} = 0) and illuminated conditions. The electrical response of devices were first analyzed under dark conditions to assess the saturation density current (J_0) and ideality factor (n), R_s and R_p (in this case the illumination condition implicit in the ISOS-L1 protocol is temporarily interrupted during this J-V characterization). Immediately after this characterization under dark condition, the devices were again characterized but now under illumination conditions (Krippelen and Brédas, 2009). The stress of continuous illuminations degraded the OPVs with the following changes in their electrical parameters: (i) J_0 increases; (ii) R_s increases; and (iii) R_p decreases (except for large area OPVs tested in dark condition). Table 2 indicates the ratio between the final value at 24 h and the initial value at 0 h (depicted as ratio 24 h/0 h) for each of these parameters. Clearly, these changes are more pronounced for small area devices. The trends observed in the changes of R_s and R_p are consistent with the reduced degradation of the FF for OPVs with scaled area, shown in Fig. 3c (lower R_s values and higher R_p values favor good charge extraction and small current leaks). Small increments of the saturation current J_0 during illumination is also desirable (high values of J_0 might limit voltages), as it occurs for the case of scaled area devices. The extracted value of the ideality factors n for both areas, resulted above the unity and exhibit a similar increment (~1.3 times) during the stability test, indicating a proportional increase of recombination losses perhaps associated to trap-assisted processes in the active films after photo-degradation (Cowan et al., 2011; Kirchhart et al., 2011).

Photo-degradation effects were also tracked through impedance spectra analysis. For these measurements, the extraction of electrical parameters is performed using an equivalent circuit composed by a resistor R_s in series with a parallel bi-component system R_s-CPE (constant phase element), where CPE is a non-ideal capacitor (Barsoukov and Macdonald, 2005). Fig. 4 displays the temporal evolution of the impedance spectra at 0 V bias voltage. Graphically, the value of the series resistance R_s can be estimated roughly finding the intersection of the semicircle projection formed by data with the Z_n axis at high frequencies. The magnitude R_s is associated to ohmic resistance, i.e., contacts, wires and sheet resistances (Guerrero et al., 2013; Arredondo et al., 2016; Guerrero et al., 2012; Perrier et al., 2012). Table 3 presents the estimated parameters by fitting data of Fig. 4 using the ZView software. For small area devices, R_s increases after 24 h although the final values are small enough (~3.3 Ω cm^2). Similar trends were obtained at 0.5 V bias voltage (Fig. S4 and Table S3). In contrast to the moderate changes observed for R_s, there is a significant decrease in R_p (this value is identified by the intersection of the semicircle projection formed by data with the Z_n axis at low frequency) at the first 12 h; such decrease is associated with changes in recombination resistance or degradation of the interface charge transport process (Zhang et al., 2013). This resistance further decreases when the voltage increase (Fig. S4 and Table S3) as a consequence of increments in charge recombination (Arredondo et al., 2016), which seems to indicate that the bulk layer was degraded simultaneously by light and air exposure, as it has been reported in different works for PTB7-PCBM blends (Bartesaghi et al., 2016; Razzel-Hollis et al., 2014), and for others BDT-based conjugated polymers (Alem et al., 2012). Such losses contribute to reduce the PCE during the stability test. In the analysis of small area devices it is clear that there is a consistency in the trend observed through impedance spectroscopy and single diode model for the series and parallel resistances. In the case of scaled devices it was not possible to generate impedance spectra for fresh samples (the high current generated by these devices was out of the range that our equipment is able to measure). Nevertheless, a similar trend in the deterioration of R_s and R_p was observed at 0 and 0.5 bias voltages.

During ISOS-L1 experiments the whole active area of devices degraded homogeneously. As an example, Fig. 5 presents LBIV maps generated at 0, 12 and 24 h for a device with area of 2.25 cm^2. According to these maps, most of the active area in fresh samples has a good photovoltaic response; although in some regions the LBIV signal was somewhat more intense. Some small defects are also observed in these maps. These defects could be introduced during the deposition of the active layer by spin coating technique or the counter-electrode by doctor blade technique. Remarkably, the small domains of defects observed in fresh samples did not induce catastrophic failures (see LBIV maps at 12 and 24 h) such that after continuous illuminations the response of the whole active area degraded homogeneously.

### Table 2

<table>
<thead>
<tr>
<th>Photovoltaic area [cm^2]</th>
<th>Illumination time [h]</th>
<th>Dark condition</th>
<th>AM 1.5 condition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>J_0 [mA/cm^2]</td>
<td>R_s [Ω cm^2]</td>
</tr>
<tr>
<td>0.09</td>
<td></td>
<td>1.59</td>
<td>7.9 × 10^-8</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>1.93</td>
<td>5.5 × 10^-7</td>
</tr>
<tr>
<td>24</td>
<td></td>
<td>2.06</td>
<td>4.1 × 10^-6</td>
</tr>
<tr>
<td>Ratio (24 h/0 h)</td>
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<td>1.29</td>
<td>17.7</td>
</tr>
<tr>
<td>2.25</td>
<td></td>
<td>2.30</td>
<td>4.0 × 10^-6</td>
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<tr>
<td>12</td>
<td></td>
<td>2.53</td>
<td>1.1 × 10^-5</td>
</tr>
<tr>
<td>24</td>
<td></td>
<td>2.87</td>
<td>4.5 × 10^-5</td>
</tr>
<tr>
<td>Ratio (24 h/0 h)</td>
<td></td>
<td>1.24</td>
<td>11.2</td>
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</table>
rather marginal (a decay of only 5%) for the same stored time. Nevertheless, it must be observed that in the latter case there are notorious fluctuations in the measured current; for instance, devices exhibited a degraded photovoltaic performance at 1920 h (with $J_{sc}$ decreasing to 64% of the original value) but at 2400 h the measured value was nearly the same than in fresh sample. It was corroborated that fluctuations of the parameters $J_{sc}$, FF and PCE seen in Fig. 6 for devices of scaled areas were not associated to artifacts or experimental errors.

It is worth to mention that, while performing these studies, we observed the formation of crystalline-type micro-domains (possibly PC$_7$BM agglomerates boosted by residual solvent (Chang et al., 2011)) in some active layers without deposited counter-electrode (see Fig. S6). Such micro-domains appeared days after the active layers deposition. Analytical studies were performed. Fig. S7 shows a distribution map for defined elements (C, S, F, and O) obtained through Energy Dispersive Spectroscopy (EDS) over the scanned area of such crystalline micro-domains. EDS indicates that micro-domains are composed mostly by carbon atoms, suggesting that they can be indeed agglomerates of PC$_7$BM. Possibly, this agglomeration process is associated to the fluctuations in photovoltaic performance shown in Fig. 6, mainly for big area devices. Notice that fluctuations in $J_{sc}$ were also observed for the

<table>
<thead>
<tr>
<th>Photoactive area [cm$^2$]</th>
<th>Illumination time [h]</th>
<th>AM 1.5</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>$R_s$  [$\Omega \cdot$ cm$^2$]</td>
</tr>
<tr>
<td>0.09</td>
<td>0</td>
<td>2.0</td>
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<tr>
<td></td>
<td>12</td>
<td>2.9</td>
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<td></td>
<td>24</td>
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<tr>
<td>2.25</td>
<td>0</td>
<td>–</td>
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<tr>
<td></td>
<td>12</td>
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<tr>
<td></td>
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<td>56.2</td>
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</table>

Fig. 4. Impedance spectra measured under illuminated conditions (ISOS-L1 protocol) at 0 V bias voltage for (a) OPVs with active area of 0.09 cm$^2$ after 0 h, 12 h and 24 h, (b) devices with active area of 2.25 cm$^2$ after 12 h and 24 h. The solid lines represent the simulations parameters shown in Table 3. Inset in (a) show details of impedance spectra at the high-frequency region.

Table 3
Changes of equivalent circuit parameters obtained from impedance spectra at 0 V of DC bias during OPVs stability test under ISOS-L1 protocol.

Fig. 5. Normalized LBIV maps obtained from an active area of 2.25 cm$^2$ tested under ISOS-L1 protocol at (a) 0 h, (b) 12 h and (c) 24 h. The scale bar indicates the detected voltage signal level. Signal is normalized with respect to the maximum values obtained in maps at 0 h.
measurements under ISOS-L1 protocol (Fig. 3) but in less extent. In any case, these fluctuation effects deserve more investigation. In view of these results for the ISOS-D1 protocol, here we can say that in the overall trend, OPVs with scaled area are significantly less degraded than small area devices. As we can see in Fig. 6d, the reduction in PCE after 2400 h was 50% and 10% for small and scaled area devices, respectively. According to our results, the use of FM as top electrode and doctor blade technique for its deposition, could possibly produce an encapsulation effect or a delay in the degradation process. Nevertheless, to make a fair conclusion on this aspect, more experiments have to be carry out, i.e., the study of the encapsulating effect of a novel top electrode and under the mentioned deposition method, must be performed with similar devices (equal active blends) comprising different electrodes and tested under the same conditions.

Through an analysis of the extracted parameters from the single diode model under dark conditions (see Table 4), one notices that unlike the ISOS-L1 protocol, in the case of ISOS-D1 protocol, the ideality factor n for small and scaled area devices remains without significant changes after 2400 h of storage. Values of ideality factor larger than unity have been related with recombination losses or disorder in electronic states (Cowan et al., 2011). This fact suggests that the donor-acceptor layer has limited deterioration in the absence of light. In regards to \( J_0 \), \( R_s \) and \( R_p \) under ISOS-D1 protocol after 2400 h, the changes follow the same tendency that in ISOS-L1 protocol for a period of 24 h. In order to study OPVs under ISOS-D1 protocol with minimal disturbance, LBIV maps and impedance spectra were taken only at the initial and final test times. Regarding the analysis by impedance spectroscopy, we could only make a comparison between initial and final resistances for small area devices. Figs. S8 and S9 and Tables S4 and S5 show that in this case the series resistance \( R_s \) remains almost unchanged at 0 V bias voltage; at 0.5 V bias voltage (see Fig. S9), which is near to the maximum voltage device operation, the somewhat large increments (from 2.2 to 5.9 \( \Omega \) cm\(^2\)) indicate a possible deterioration in the contacts.

In regards to the abrupt decrease in the resistance \( R_1 \) at low

![Fig. 6. Evolution of normalized parameters (a) current density, (b) open circuit voltage, (c) fill factor and (d) power conversion efficiency for the two active areas, 0.09 cm\(^2\) (filled squares) and 2.25 cm\(^2\) (open circles) under ISOS-D1 testing protocol. The average values and error bars were calculated from the parameters obtained from six devices of 0.09 cm\(^2\) and three of 2.25 cm\(^2\).](image)

**Table 4** Evolution of the extracted electrical parameters for OPVs tested using the ISOS-D1 protocol.

<table>
<thead>
<tr>
<th>Photoactive area [cm(^2)]</th>
<th>Illumination time [h]</th>
<th>Dark condition</th>
<th>AM 1.5 condition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( n )</td>
<td>( J_0 ) [mA/cm(^2)]</td>
<td>( R_s ) [( \Omega ) cm(^2)]</td>
</tr>
<tr>
<td>0.09</td>
<td>0</td>
<td>1.61</td>
<td>5.7 ( \times ) 10(^{-8})</td>
</tr>
<tr>
<td></td>
<td>2400</td>
<td>1.68</td>
<td>3.3 ( \times ) 10(^{-6})</td>
</tr>
<tr>
<td>Ratio (2400 h/0 h)</td>
<td>–1</td>
<td>57.9</td>
<td>5.5</td>
</tr>
<tr>
<td>2.25</td>
<td>0</td>
<td>1.77</td>
<td>1.1 ( \times ) 10(^{-7})</td>
</tr>
<tr>
<td></td>
<td>2400</td>
<td>1.78</td>
<td>2.7 ( \times ) 10(^{-6})</td>
</tr>
<tr>
<td>Ratio (2400 h/0 h)</td>
<td>–1</td>
<td>24.5</td>
<td>1.4</td>
</tr>
</tbody>
</table>
frequencies, it is interpreted as a degradation of the interlayer between BHJ/ETL (PTB7:PC71BM/PFN) and the metal counter-electrode (FM) induced possibly by the presence of moisture and oxygen. In absence of light, the film stack has been affected to a greater extent by moisture and oxygen at the device edges, as it was observed by LBIV (see Figs. S10 and S11). It is observed that for fresh devices there is a reduction in the photovoltaic response from the edges toward the center (edges are in direct contact with the environment and then to direct exposure to moisture and oxygen); this particular effect is evident for small area devices. Histograms of the number of pixels exhibiting certain level of voltage from LBIV maps can be consulted in Figs. S10 and S11.

Finally, our results can be discussed in the context of other stability tests performed for PTB7:PCBM-based OPVs under the ISOS-D1 protocol. Kim et al. (2015) investigated the correlation between performance and morphology and the influence of the additive DIO in OPVs with the configuration: ITO/PEDOT:PSS/PTB7:PC71BM/TiOx/Al. In optimized devices with active area of 0.11 cm², they reached an average PCE of 7.76 ± 0.07% that was reduced in 50% (3.02 ± 0.04) after 300 h (Ts = 300 h) by testing devices under normal air conditions. In other investigation, Abdel-Fattah et al. (2015) studied the enhancement in stability and efficiency introduced by TiOx layer in the architecture: ITO/PEDOT:PSS/PTB7:PC71BM/TiOx/Al. In this case the study showed that in OPVs with 0.1 cm² of active area the PCE decrease was 98% and 41% from the initial PCE value (2.8%) for non-encapsulated and encapsulated devices after 20 days of storage in air, respectively. Very recently, Sanchez et al. (2017) reported the stability of the conventional architecture: ITO/PEDOT:PSS/PTB7:PC71BM/Ca/Ag and the inverted one: (ITO/TiOx/PTB7:PC71BM/V2O5/Ag), with initial PCE average values of 7.43 ± 0.07% and 8.25 ± 0.16%, respectively. They demonstated that under nitrogen atmosphere the Ts = value for PCE in conventional and inverted OPVs (0.09 cm² of active area) is reached at 1200 and 6048 h, respectively. Nevertheless, when the inverted devices were exposed to normal air conditions Ts = was reached at 120 h for encapsulated devices and 5 h for non-encapsulated cells. In these three cited works (Kim et al., 2015; Abdel-Fattah et al., 2015; Sanchez et al., 2017), the counter-electrodes consisted of metals deposited by standard vacuum-evaporation techniques. Thus, in view of the results of these cited works, our PTB7:PCBM-based OPVs, comprising the alloy FM (of low melting point) as counter-electrode and deposited by doctor blade technique, showed a competitive shelf lifetime. This fact can result of interest for the search of alternative counter-electrodes of easy deposition at low cost. According to the results, the lifetime for our OPVs in direct contact with ambient conditions, although poor in comparison with other reported polym-mer:fullerene blends (Djurisic et al., 2016; Cheng and Zhan, 2016) is mostly determined by the intrinsic instability of PTB7:PC71BM blend and not by instabilities introduced by the counter-electrode.

4. Conclusions

Photovoltaic performance and stability of PTB7:PC71BM based solar cells were investigated when the active area is scaled from 0.09 cm² to 2.25 cm² (a PCE reduction of ∼60% is observed). Although there is a considerable decrease in some of the electrical parameters that characterize the device performance after scaling the sizes of active layers and electrodes, most of the series resistive effects can be ascribed to the increase of the indium tin oxide (ITO) sheet resistance, i.e., FM does not change considerably the device resistance after scaling. Losses due to lack of homogeneity and defects introduced during organic layers deposition also reduce photovoltaic performance. However, it is still possible to improve fabrication conditions and propose new alternatives like the use of sub-electrodes to reduce series resistance from ITO. Our results show that in presence of light, the photo-degradation triggered by the presence of oxygen and moisture remains independent of the active area. However, in absence of light, scaled area devices tend to be more stable. Remarkably, FM does not introduce extra instabilities in OPVs such as in devices with aluminum top electrode.

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Appendix A. Supplementary material

Specification of test protocols and supplementary current density-voltage curves, impedance spectra and LBIV graphs and data. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.solener.2018.01.090.

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